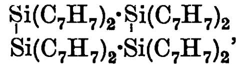
CCCXL.—*Organic Derivatives of Silicon. Part XLI. Octa*-p-*tolylsilicotetrane, Octa*-p-*tolyl*cyclo*silicotetrane, and Other Products from Di*-p-*tolylsilicon Dichloride.*

By Alfred Raymond Steele and Frederic Stanley Kipping.

As many interesting results have been obtained from an investigation of the action of sodium on diphenylsilicon dichloride (Kipping and Sands, J., 1921, **119**, 330; Kipping, J., 1924, **125**, 2291; 1927, 2719), a study of the behaviour of di-*p*-tolylsilicon dichloride (Pink and Kipping, J., 1923, **123**, 2832) under like conditions has been commenced. So far the experiments have shown that to some extent, at least, the two dichlorides react in a similar manner, since the ditolyl derivative, in toluene solution, gives *octa*-p-*tolylsilicotetrane*, $[Si(C_7H_7)_2]_4$, containing two tervalent silicon atoms, and *octa*-p-*tolyl*cyclo*silicotetrane*,  $\begin{array}{l} Si(C_7H_7)_2\cdot Si(C_7H_7)_2 \\ | \qquad\qquad\quad | \\ Si(C_7H_7)_2\cdot Si(C_7H_7)_2 \end{array}$, which correspond respectively to the open-chain and closed-chain octaphenyl derivatives (A and B).

The open-chain compound is more readily soluble than its phenyl analogue; it combines with iodine at the ordinary temperature, giving a crystalline *di-iodide*, $Si_4(C_7H_7)_8I_2$, and from the latter, by hydrolysis, there is easily formed a well-defined *oxide*, $Si_4(C_7H_7)_8O$, which has a sharp melting point and does not show the unaccountable behaviour of the corresponding phenyl derivative (J., 1921, **119**, 840). The open-chain compound readily undergoes fission with piperidine and alkali, giving di-*p*-tolylsilicanediol; its investigation in other directions has not yet been undertaken.

Octa-*p*-tolyl*cyclo*silicotetrane crystallises well and is very similar to the cyclic phenyl compound, being stable towards iodine and much more resistant to fission than its open-chain isomeride; so far no derivatives have been obtained from it, but it would seem that, like octaphenyl*cyclo*silicotetrane, it can assume an unstable amorphous form readily soluble in cold acetone; this matter will be further investigated.

In addition to the two well-defined crystalline compounds referred to above, another solid is produced in very small proportion from the ditolylsilicon dichloride. This product is practically insoluble in boiling benzene and all other solvents which were tried; it seems to be amorphous and to have the composition $[Si(C_7H_7)_2]_n$; it is not attacked by piperidine and aqueous alkali. It differs, therefore, in important respects from the well-defined, crystalline, very sparingly soluble compound C, which is obtained from diphenylsilicon dichloride and also from the insoluble amorphous product D, which so readily undergoes fission.

The main product of the interaction, like that (E) from diphenylsilicon dichloride, is readily soluble in cold acetone. When fractionated systematically, it gave a graded series of amorphous powders melting indefinitely from about 120° downwards. It was at first presumed that this material corresponded to E, and consisted chiefly of an amorphous form of octatolyl*cyclo*silicotetrane, but the results of analysis pointed to the presence of about $1\frac{1}{2}\%$ of oxygen and the hydrogen values were at least 20% lower than those calculated for $Si_4(C_7H_7)_8 + 8H_2O = 4Si(C_7H_7)_2(OH)_2 + 4H_2$. All the fractions examined seemed to have practically the same composition and all the data corresponded approximately to those required for the oxide $Si_4(C_7H_7)_8O$, but as the latter is a well-defined compound, m. p. 228—229°, its chemical identity with this amorphous product seems to be improbable. Further, in an experiment in which xylene was used as solvent for the dichloride, and the heating with sodium occupied 30 hours, the results were very different from those obtained in toluene solution; there was no insoluble solid, neither of the octatolyl derivatives could be isolated, and the whole of the product was soluble in cold acetone. Even in different experiments with toluene the actual and relative yields of the two crystalline products were very different. Further investigation is necessary, therefore, in many directions and will be undertaken in the immediate future; the publication of the results so far obtained is unfortunately necessitated by the usual circumstances attending a joint investigation.

EXPERIMENTAL.

Preparation of Di-p-*tolylsilicon Dichloride.*—The samples of dichloride prepared by Pink and Kipping (*loc. cit.*) contained at least 7% of impurity which was thought to be ditolyl; as it was necessary to start with pure material in this investigation, the preparation was carried out as described by Kipping and Murray (J., 1927, 2734) in the case of diphenylsilicon dichloride. Systematic fractionation of the crude product gave a liquid (yield, about 30% of the theoretical), b. p. 237—239°/50 mm. [Found: Cl, 25·4, 25·0. Calc. for $Si(C_7H_7)_2Cl_2$: Cl, 25·3%]. The lower boiling point of the preparations collected previously was no doubt due in part to the presence of ethoxy-derivatives as well as ditolyl, since the lower fractions obtained even by the improved method gave ethyl alcohol on hydrolysis.

Action of Sodium on the Dichloride.—A solution of the pure dichloride (20 g.) in about 20 volumes of dry toluene was heated with a considerable excess (about 10 g.) of clean sodium in an atmosphere of dry nitrogen. The reaction commenced at about the melting point of the metal and changes very similar to those in the case of the diphenyl derivative were observed, the deposit of sodium chloride being of a deep blue colour. After about 10 hours' boiling, when a filtered sample seemed to give a neutral reaction to moist litmus and to contain no chlorine, the solution was filtered, and the solvent evaporated under diminished pressure; when cold, the residue of crystals and glue-like matter was treated with cold acetone and the undissolved products (3—4 g.) were separated by filtration. The acetone solution on evaporation gave a glue-like material (p. 2549) and the dark blue mineral residue afforded an amorphous insoluble substance (p. 2549).

Octa-p-*tolylsilicotetrane.*—The crystalline residue, undissolved by cold acetone, was fairly readily soluble in hot benzene or hot chloroform and by fractionation from either of these solvents mixed with acetone it was separated into two well-defined crystalline compounds. *Octa*-p-*tolylsilicotetrane*, the more sparingly soluble one, crystallised from benzene or from chloroform–acetone in small, six-sided prisms melting at 290—293°, apparently with slight decomposition, since the cooled substance liquefied again at a lower temperature and, if kept fused during a short time, afterwards solidified to a transparent resin. It was very slightly soluble in boiling alcohol, acetone, and acetic acid and only sparingly soluble in cold benzene [Found: Si, 13·6; M, cryoscopic in camphor, 805. $Si_4(C_7H_7)_8$ requires Si, 13·4%; M, 840].

The compound gave hydrogen readily with a mixture of aqueous alkali and piperidine; 1 g. gave 105·5 c.c., the theoretical value for complete fission being 107 c.c. When the piperidine was removed by steam distillation, the alkaline solution gave a colourless deposit which was crystallised from chloroform–light petroleum and identified as trianhydrotrisdi-*p*-tolylsilicanediol. Further evidence in support of the given molecular formula is afforded by the results of the titrations with iodine.

Octa-p-*tolylsilicotetrane Di-iodide*, $Si_4(C_7H_7)_8I_2$.—Octa-*p*-tolylsilicotetrane was covered with dry benzene and a solution of iodine in dry benzene was run in gradually until a permanent coloration was obtained which corresponded to the disappearance of the last portion of crystalline matter. The solution was warmed at about 50° merely to hasten the dissolution of the sparingly soluble silicon compound [0·538 g. combined with 0·156 g. of iodine. Required for $Si_4(C_7H_8)_8$: I, 0·162 g.]. The clear benzene solution was evaporated under reduced pressure and the residue, a pale yellow oil, was treated with dry ether; the *di-iodide* was immediately precipitated in colourless crystals, which were rapidly washed with dry ether, in which they were very sparingly soluble, and then freed from solvent under reduced pressure. A weighed quantity was hydrolysed with ammoniacal acetone and the iodide in the aqueous solution was estimated [Found : I, 23·4. $Si_4(C_7H_7)_8I_2$ requires I, 23·2%].

The di-iodide appears to be fairly stable in the solid state, but its solution in benzene or ether soon turns brown on exposure to air and light. It is very readily soluble in cold benzene and crystallises well from ether–benzene in rhomboidal plates, m. p. about 300° (decomp.).

Octa-p-*tolylsilicotetrane Oxide*, $Si_4(C_7H_7)_8O$.—A pure sample of the di-iodide was warmed on a water-bath during a short time with aqueous acetone; the washed product, when recrystallised several times from boiling acetone, was obtained in well-defined six-sided prisms, m. p. 228—229° [Found : Si, 13·3; hydrogen value, 75. $Si_4(C_7H_7)_8O$ requires Si, 13·1%; hydrogen value, 78]. It is readily soluble in boiling acetone or chloroform, moderately easily soluble in boiling benzene, and very sparingly soluble in alcohol or acetic acid; it readily undergoes fission with piperidine and aqueous alkali. That the substance is the *oxide* and not the dihydroxide seems to be shown by the results of the silicon determination, since the diol requires Si, 12·9%. Except for the formation of a relatively very small amount of an apparently amorphous powder, insoluble in all common solvents, the di-iodide appears to be converted quantitatively into the oxide on hydrolysis; this fact and the well-defined properties of the oxide contrast with the observations made in the case of the corresponding phenyl derivative.

Octa-p-*tolyl*cyclo*silicotetrane*, $[Si(C_7H_7)_2]_4$.—This cyclic *compound* is separated from its open-chain isomeride by repeated fractionation from acetone–chloroform. It melts fairly sharply at 310°; its purity was also established by microscopical investigation [Found : Si, 13·3; hydrogen value, 104; *M*, cryoscopic in benzene, 765. $Si_4(C_7H_7)_8$ requires Si, 13·4% ; hydrogen value, 107; *M*, 840].

Octa-*p*-tolyl*cyclo*silicotetrane is readily soluble in cold benzene and chloroform, but not so freely as the corresponding phenyl compound, and crystallises from either of these solvents, mixed with acetone, in large, highly refractive, rhomboidal prisms. When rapidly deposited from cold benzene, it forms thin, six-sided plates, many of which are regular hexagons in outline; but when slowly evaporated, the solution gives large transparent prisms which contain solvent and become opaque on exposure to the air. It is only very sparingly soluble in cold acetone, alcohol, acetic acid, and ethyl acetate. Its benzene solution does not absorb iodine and it is unchanged when it is boiled with tetrachloroethane or with nitrobenzene during long periods. With piperidine and caustic soda it gives hydrogen only very slowly even at about 100°, but finally it is completely converted into di-*p*-tolylsilicanediol or its condensation products.

The easiest way of obtaining a specimen of the cyclic compound entirely free from the open-chain isomeride is to treat the mixture with a slight excess of iodine in benzene solution and then to boil the product with aqueous acetone; the oxide which is thus formed from the unsaturated compound is readily separated from the silicohydrocarbon by extraction with hot acetone.

Resinous Product.—The acetone extract of the original product was separated by fractional precipitation with alcohol into about 12 fractions; a portion of each fraction was then submitted to further treatment with various solvents, but no crystalline product was obtained. The original fractions were colourless amorphous powders except the glue-like, most soluble portion; they were all readily soluble in most of the common solvents with the exception of alcohol, acetic acid, and light petroleum. Some of the more sparingly soluble fractions were kept under reduced pressure until constant in weight and then examined:

Fraction.	M. p.	C.	H.	Si.	H_2 value.
I	120—135°	79·0	6·8	12·7	84
III	100—128	79·1	6·7	12·8	82
VI	95—120	79·1	6·8	12·6	81

Calc. for $Si(C_7H_7)_2$: C, 80·0; H, 6·6; Si, 13·3%; hydrogen value, 107.

Calc. for $Si_4(C_7H_7)_8O$: C, 78·5; H, 6·5; Si, 13·1%; hydrogen value, 78.

All these data agree fairly well with those required for a mixture of the oxide $Si_4(C_7H_7)_8O$ with a small proportion of some material poorer in silicon, but such a view of the nature of this product can hardly be accepted.

Amorphous Insoluble Product.—The blue residue of sodium chloride and unchanged metal (p. 2547) was well washed with hot toluene and then cautiously added to a mixture of alcohol and excess of acetic acid; water was added to the colourless or pale blue mixture and the grey flocculent material left in suspension was separated by filtration and exhaustively washed with water. The product (0·5—1 g. from 20 g. of dichloride) appeared to be practically insoluble in all the solvents which were tried, including boiling aniline, phenol, and nitrobenzene; when extracted with boiling benzene during 30 hours, it afforded only a very small proportion of soluble matter. The residue was a colourless amorphous powder which charred at a high temperature, without melting [Found: Si, 13·1. Calc. for $Si(C_7H_7)_2$: Si, 13·3%]. It gave no hydrogen with aqueous alkali and piperidine and did not seem to react with iodine in benzene solution.

Experiment in Xylene Solution.—In a second experiment with the pure dichloride (30 g.) and excess of sodium in boiling xylene solution in an atmosphere of nitrogen, the liquid acquired a reddish-brown colour at the end of about 4 hours. Samples then exposed to the air quickly became pale yellow and still gave an acid reaction to moist litmus. The boiling was therefore continued, the filtered reddish-brown solution being tested every 4 hours or so, but it was not until 30 hours had elapsed that the filtrate was free from chlorine; it then gave a slightly alkaline aqueous extract. The filtered xylene solution, acidified with acetic acid and evaporated under reduced pressure, gave a glue-like mass completely soluble in cold acetone and apparently free from both octatolyl derivatives; further, the saline residue gave no product insoluble in water.

The whole of the soluble material was separated as before into six fractions. About 0·1 g. of sodium acetate was isolated from the most soluble fraction, and the less soluble fractions afforded a very small proportion of a colourless flaky material (Found: Si, 9·8; C, 80·6; H, 7·1%), insoluble in acetone, which gave hydrogen with piperidine and alkali.

Analyses of some of the main fractions (I was the most sparingly soluble) gave the following results:

Fraction.	M. p.	C.	H.	Si.	Hydrogen value.
I	Up to about 120°	82·6	6·8	10·3	0
II	„ „ 100	—	—	—	—
III	„ „ 95	81·3	7·1	10·2	33
V	—	80·3	7·0	—	30
VI	Oil	—	—	10·8	—

It will be seen that this amorphous soluble product differs materially from that obtained in toluene solution and the low percentage of silicon indicates the presence of compounds containing the group $Si(C_7H_7)_3$.

In a third experiment, with toluene, the sodium was melted in nitrogen and filtered through glass wool directly into the reaction flask; the products were similar to those obtained in the first place, but the proportion of cyclic to open-chain compound was approximately 2 : 1, instead of 1 : 2 as in the first experiment.

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UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, August 27th,* 1929.]